MECHANISMS FOR PERFORMANCE ENHANCEMENT OF Bi2Te3 IN POLYMER COMPOSITES

By

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Abstract

We demonstrated the use of the as-received conjugated polymer P3HT (poly (3-hexylthiophene-2,5 diyl) doped with F4TCNQ (2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) as a matrix for forming a composite with as-received, commercially available p-type Bi_2Te_3 powder. The optimized formulation, containing no small inorganic ions, exhibits a power factor of up to $5.3\ uW\ K^{-2}\ m^{-1}$, about nine times higher than the highest power factor we achieved from mixtures of only P3HT and F4TCNQ. The Bi_2Te_3 was responsible for increases in both Seebeck coefficient and electrical conductivity. P3HT, with higher hole mobility, was superior to PQT12 (poly(bisdodecylquaterthiophene), and F4TCNQ was superior to $FeCl_3$, for matrix and dopant, respectively, for this purpose. The power factor obtained is about 40% of that reportedly obtained from synthesized Bi_2Te_3 nanowires in $FeCl_3$-doped P3HT. Thus, a doped conjugated polymer system made only from commercial-grade components was shown to support the extraction of thermoelectric performance by a commonly used inorganic semiconductor.

Advisor: Howard E. Katz

Contents

1.Introduction

The relationship of energy conversion for thermoelectric performance is

$$ZT = S^2\sigma T/\kappa$$

where S is the Seebeck coefficient (also known as thermopower, the change in voltage with the change in temperature), σ is the electrical conductivity, T is the temperature in Kelvin and κ is the thermal conductivity.[1] The power factor P incorporates Seebeck coefficient and electrical conductivity; the exactly relation is $P = S^2\sigma$. While the original thermoelectric materials, such as Bi_2Te_3, are inorganic, organic materials have recently been considered because of their potential printability, mechanical flexibility, and use of earth-abundant elements.[2] Many of the latter materials are conjugated thiophene polymers, including the prototypes poly (3-hexylthiophene-2,5 diyl) (P3HT) and poly(3,3'''-didodecyl quarter thiophene) (PQT-12). While in special cases, power factors of about 10 $uW\,K^{-2}\,m^{-1}$ can be obtained from all-organic systems,[3] values of 1 $uW\,K^{-2}\,m^{-1}$ are more typical.[4] Thus, it is attractive to use polymers as matrices in which the higher performance characteristics of the inorganic materials can be captured.

Bi_2Te_3 has been used in composites with the conducting polymer composition known as PEDOT-PSS (poly(ethylenedioxythiophene) polystyrenesulfonate).[5]

While strictly speaking, this is a doped thiophene polymer, result on such composites, including from our own group, did not take into account the more recently appreciated complication that some of the thermoelectric response could be due to mobile ions, such as protons, in the formulation.[6] Thus, it is desirable to characterize Bi_2Te_3 composites in conducting polymer matrices that do not incorporate mobile ions such as the sulfonic acid protons of PSS. Several years ago, there was a report of achieving a high power of about 13.6 $uW\,K^{-2}\,m^{-1}$ by mixing synthesized Bi_2Te_3 nanowires into synthesized P3HT doped with $FeCl_3$.[7] Neither the polymer or the inorganic semiconductor are generally available from commercial sources, and the dopant is not soluble in solvents compatible with the polymer, decreasing some of the cost and processing advantages of the organic composites and making it difficult to quantify the introduced dopant. Thus, we were motivated to characterize related systems using a solvent-compatible dopant and all-commercial material sources. In this work, we used commercial P3HT, commercial Bi_2Te_3 powder, and the organic dopant F4TCNQ. With this material set, we observe the pronounced contribution of the Bi_2Te_3. The highest power factor we obtained, about $5.3\,uW\,K^{-2}\,m^{-1}$, is 40% of the value that was reported by He et al. for the specifically synthesized nanowire-polymer combination. The influence of charge carrier mobility of the matrix polymer on the composite performance was also shown.

2. Experimental Section

2.1 Materials

Commercial P3HT (poly (3-hexylthiophene-2,5 diyl)), typical Mw=50-70KDa, PD=1.4-1.6, was purchased from Solaris Chem Inc. Commercial PQT12 (poly(3,3‴-didodecylquaterthiophene)) was purchased from Solaris Chem Inc. Commercial F4TCNQ (2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane), was purchased from Ossila. Commercial Bi_2Te_3, powder, 99.99% trace metals basis, was purchased from Sigma Aldrich.

2.2 Sample Preparation

The P3HT powder was dissolved into chlorobenzene with a concentration of 10 mg (P3HT)/ml (chlorobenzene). F4TCNQ was dissolved into chlorobenzene with a concentration of 2 mg (F4TCNQ)/ml (chlorobenzene). The P3HT solution was heated on a hot plate at 45 °C for 30 minutes. The F4TCNQ solution was heated on a hot plate at 60 °C for 30 minutes. The two solutions were combined, with further heating at 60 °C for 30 minutes. Bi_2Te_3 powder was added directly into the mixed solution, which was then heated at 60°C for 1h.

The solution was dropcast onto a glass substrate with 2 gold electrodes on it. The glass substrate was pre-cleaned with deionized water, acetone and 2-propoal. The gold electrodes were made by thermal evaporation and their thickness was 50 nm. The effective sample area was 0.7 cm long, 0.9 cm wide. The width of gold electrodes and that of the space between the 2 electrodes was 0.3 cm. After most of the solvent was

evaporated from the dropcast films, they were baked at 60 °C in a nitrogen filled glove box. Above that temperature, we found significant electronic property degradation.

2.3 Characterization

Film thickness was measured using a laser microscope. Surface roughness was characterized using scanning electron microscopy (SEM). S and σ were measured using techniques previously described.[8]

3. Results and Discussion

We first checked the thermoelectric performance of pure commercial P3HT, which was very poor. The typical conductivity was 10^{-4} S/cm and S was about 800 μV/K, for a power factor of about 0.01 $\mathrm{W\,K^{-2}\ m^{-1}}$. We then characterized P3HT with F4TCNQ with a weight ratio of 2:1, (66.6%(P3HT):33.3%(F4TCNQ)) (Table 1).

Table 1. P3HT/F4TCNQ: average power factor: 0.56 $u\,W/m\,K^2$, standard deviation: 0.39, highest :0.93

Weight ratio	Seebeck coefficient (uV/K)	Conductivity (S/cm)	power factor ($u\,W/m\,K^2$)
#1 2:1	48.6	3.95	0.93
#2 2:1	22.3	3.3	0.16
#3 2:1	43.8	3.04	0.58

This is the best ratio we have found to achieve the highest thermoelectric performance. The conductivity was 3 S/cm and S was 44 μV/K, for a power factor of

$0.6\ \mathrm{W\ K^{-2}\ m^{-1}}$, typical for a doped polymer with moderate charge carrier mobility.[9]

The correspondence of the two measurements is shown in Figure 1.

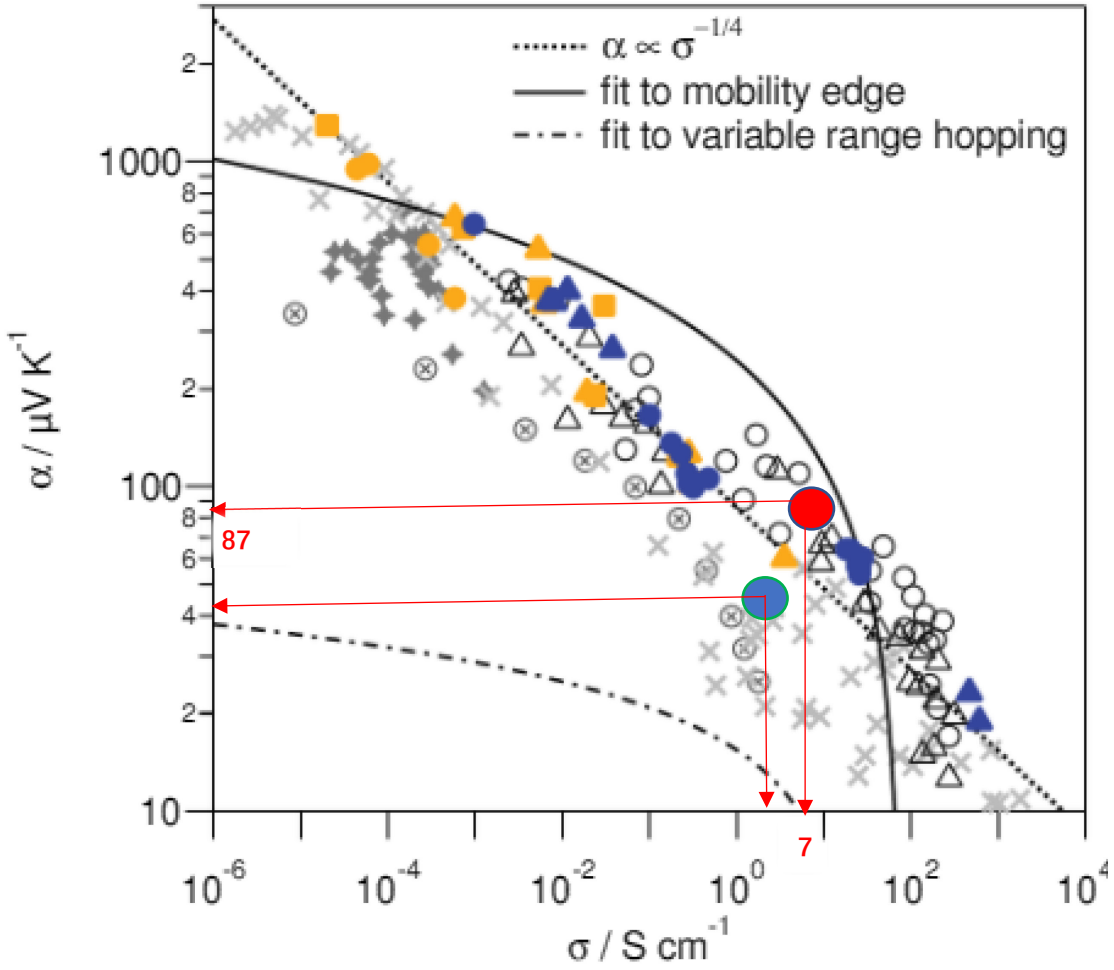
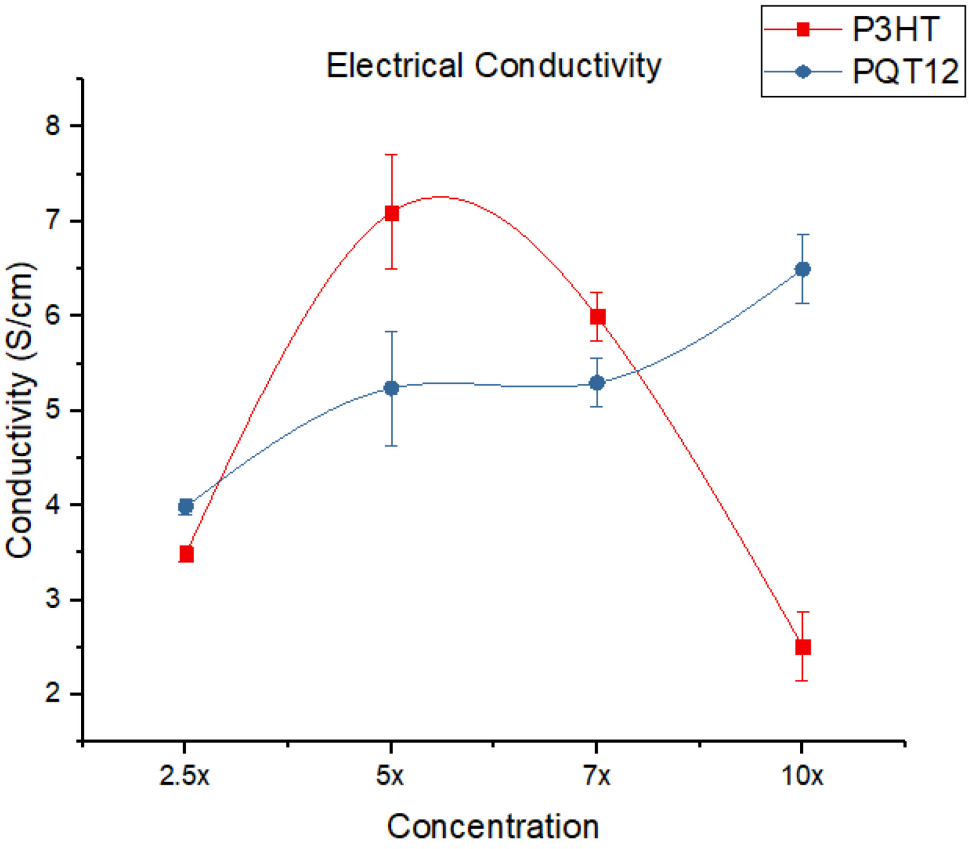
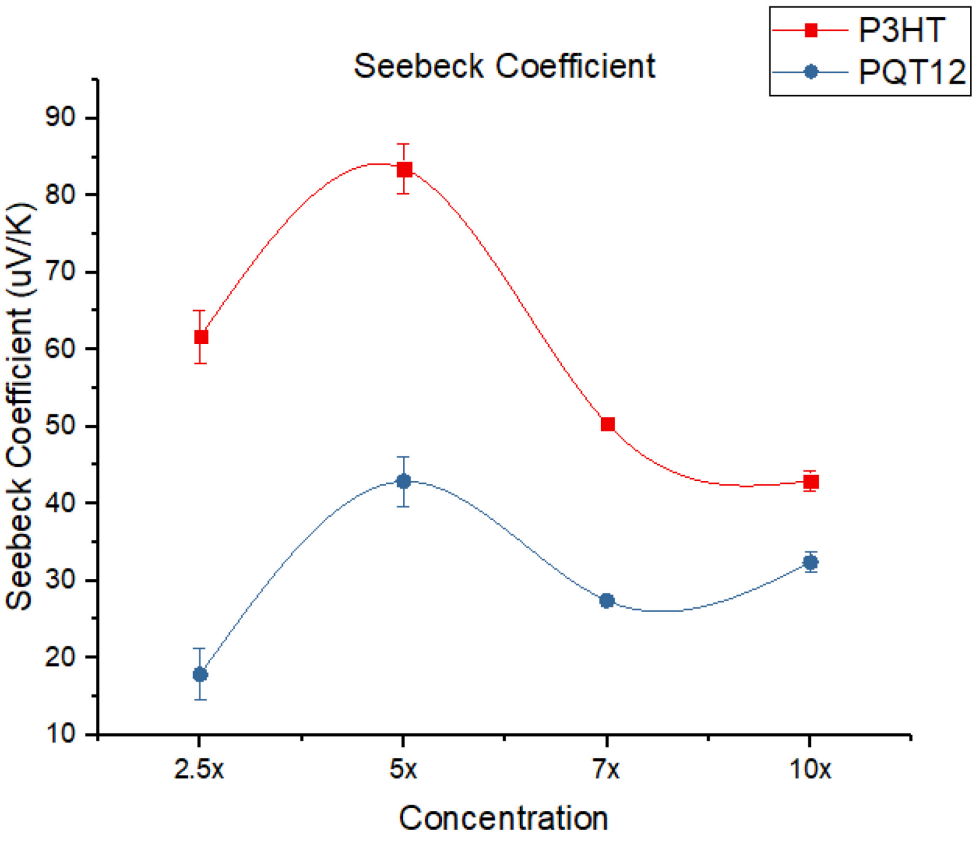


Figure 1. Position of doped P3HT, with (red) and without (blue) Bi_2Se_3, on the S-σ plot of Chabinyc (ref. 8).

We added Bi_2Te_3 at different weight ratios into the P3HT-F4TCNQ solution. Thermoelectric parameters are listed for these ratios in Table 2. The evolution is also shown graphically in Figure 2.


Electrical Conductivity
P3HT
PQT12
Conductivity (S/cm)
8
7
6
5
4
3
2
2.5x
5x
7x
10x
Concentration


Seebeck Coefficient
P3HT
PQT12
Seebeck Coefficient (uV/K)
90
80
70
60
50
40
30
20
10
2.5x
5x
7x
10x
Concentration

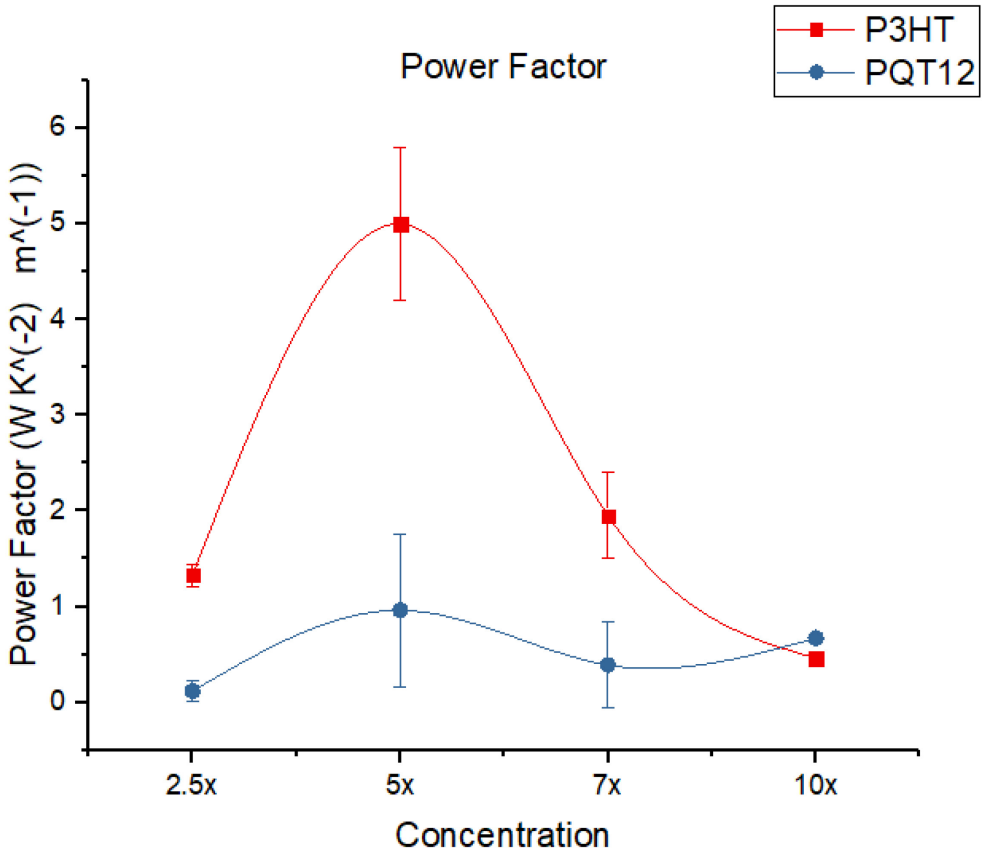


Figure 2. Evolution of power factor with increasing addition of Bi_2Te_3 to polymer and F4TCNQ in 2:1 ratio. The multiples along the x-axis refer to the relative amounts of Bi_2Te_3 to the combined organics.

Table 2. P3HT-F4TCNQ-Bi_2Te_3 Composite Properties

Weight ratio	Seebeck coefficient (uV/K)	Conductivity (S/cm)	power factor $(u\,W/m\,K^2)$
2:1:5	58.3	3.57	1.21
2:1:10	86.7	7	5.35
2:1:14	62	6.25	2.4
2:1:20	44	1.17	0.23

The order of the weight ratio is P3HT:F4TCNQ: Bi_2Te_3.

We found that the best ratio for the 3 materials is 2:1:10 (weight ratio, P3HT:F4TCNQ: Bi_2Te_3) or 15% polymer, 8% dopant and 77% Bi_2Te_3, where we achieved a power factor of 5.3 $u\,W/m\,K^2$. This was about 9 times higher than the

P3HT/F4TCNQ device. This conclusion is based on three P3HT/F4TCNQ devices and three P3HT/F4TCNQ/Bi_2Te_3 devices (Table 3). As the ratio of Bi_2Te_3 to P3HT goes over 5:1, the thermoelectric performance of the composite starts to decrease. This seems to be because too much Bi_2Te_3 powder will compromise the integrity and continuity of the composite, creating highly resistive interruptions. This deleterious effect was visualized by SEM images shown in Figure 3.

Figure 3a:
PQT12-F4TCNQ-Bi_2Te_3

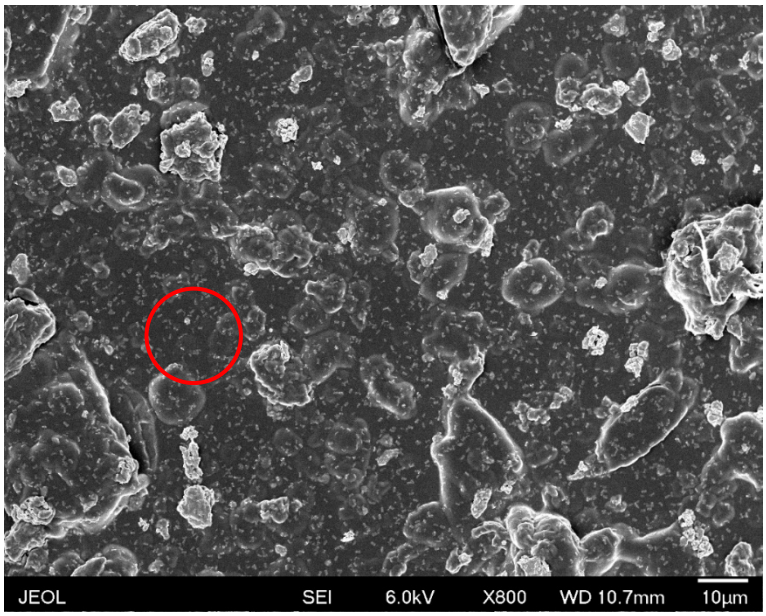
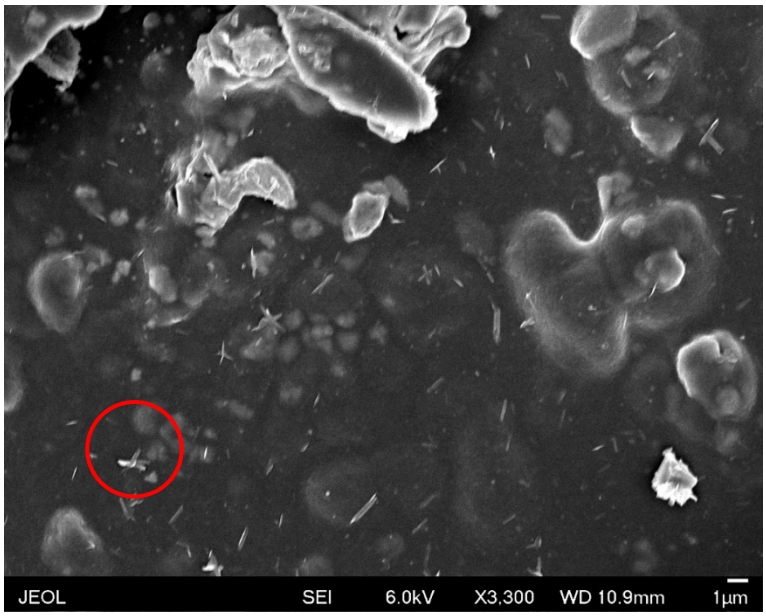


Figure 3b:
P3HT-F4TCNQ-Bi_2Te_3



From the scanned pictures we can see that the white dots uniformly distributed on the film should be the Bi_2Te_3 particles.

Table 3. P3HT/F4TCNQ/Bi_2Te_3: average power factor: 4.2 $u\,W/m\,K^2$, standard deviation: 1.02, highest: 5.35

Weight ratio	Seebeck coefficient (uV/K)	Conductivity (S/cm)	power factor ($u\,W/m\,K^2$)
#1 2:1:10	66.3	7.69	3.38
#2 2:1:10	86.8	7	5.35
#3 2:1:10	80.3	6.03	3.89

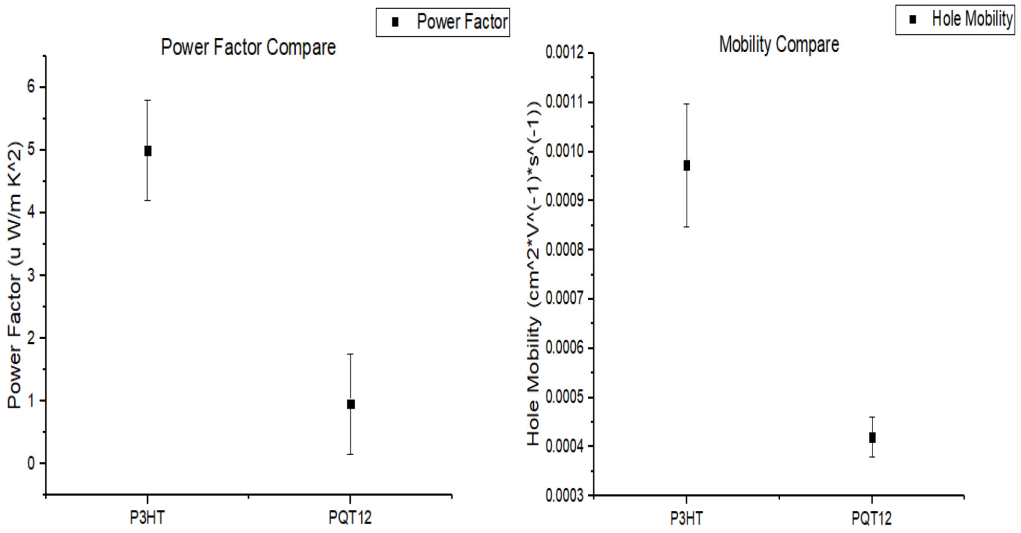


Figure 4. Graphical comparison of composite power factor and polymer hole mobility of P3HT and PQT12.

When we used PQT-12 in these doped composite formulations instead, we achieved a power factor of 0.96 $u\,W/m\,K^2$. This is also ~9 times higher than what we obtained from PQT-12 and F4TCNQ composite, but not quite as high as for the P3HT samples, as shown graphically in Figure 4.

We spincoated coat pure P3HT/PQT-12 onto 300 nm SiO_2 wafers and vapor-deposited gold electrodes to form field-effect transistors. Mobilities measured from these devices are shown in Table 4.

Table 4. Mobility Measurements from Field-effect Transistors.

Sample number	Unit $(cm^2 * V^{-1} * s^{-1})$
P3HT #1	0.0011
P3HT #2	0.00097
P3HT #3	0.00085

Sample average: 0.000973, standard deviation: 0.000125

Sample number	Unit $(cm^2 * V^{-1} * s^{-1})$
PQT-12 #1	0.00038
PQT-12 #2	0.00047
PQT-12 #3	0.00044
PQT-12 #4	0.0004

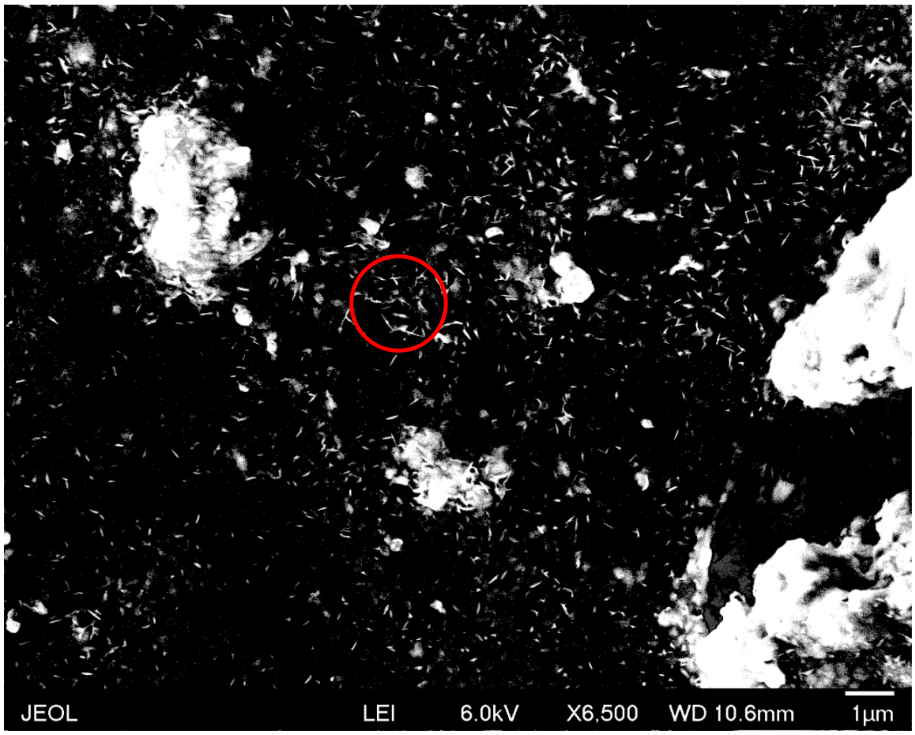
Sample average: 0.00042, standard deviation: 0.0000403

We also performed the experiment analogous to the study that used $FeCl_3$ and Bi_2Te_3 nanowires in P3HT. We doped P3HT with $FeCl_3$, with a weight ratio of 30-33% $FeCl_3$ to P3HT. Because $FeCl_3$ is only slightly soluble in chlorobenzene, we also made a comparison experiment to check if there is difference between adding $FeCl_3$ powder directly into the P3HT solution and adding $FeCl_3$ solution (in ethanol) into the P3HT solution. We also added Bi_2Te_3 powder into the solution. The highest thermoelectric performance we obtained from $FeCl_3$ doped P3HT is 24 uV/K for Seebeck coefficient and 27 S/cm for electrical conductivity. A power factor of 1.56 uW/mK^2 was achieved from these data. The highest thermoelectric performance we obtained from $FeCl_3$ doped P3HT with Bi_2Te_3 powder is 43 uV/K for Seebeck coefficient and 21 S/cm for electrical conductivity (Table 5). A power factor of 3.81 uW/mK^2 was achieved from these data. SEM of this sample is shown in Figure 5.

Table 5. Thermoelectric performance of $FeCl_3$ dope P3HT with Bi_2Te_3 powder.

Type	Seebeck coefficient (uV/K)	Conductivity (S/cm)	power factor $(u\,W/m\,K^2)$
powder	34	16	1.9
solution	43	21	3.8

Figure 5:
P3HT-$FeCl_3$-Bi_2Te_3



4. Conclusion

We demonstrated that thermoelectric contributions of as-received Bi_2Te_3 powders are obtainable in mixtures of commercially available conjugated polymers and dopants. Compared with reference 5 published in *Energy & Environmental Science*, the major differences are the dopant and the Bi_2Te_3 powder we used. The dopant F4TCNQ results in lower conductivity than $FeCl_3$, and our results show that the highest conductivity of P3HT/F4TCNQ composite is 3.95 S/cm, compared to 21 S/cm from P3HT/$FeCl_3$ composite, consistent with expectations. We believe that the major enhancement in the prior work is due to the Bi_2Te_3 nanowires. Compared with powder, nanowire has a more crystalline and interconnected structure. This usually results in better alignment and better conductivity. From the combined results from our work and reference 5, we found

out that our Seebeck coefficient value are similar, ~80-100 uV/K, which is reasonable because we both used the same material. But our conductivity only reached 7 S/cm while theirs reached 18 S/cm. Additionally, our results offer a new combination of organic/inorganic campsites which can show very good thermoelectric performance without using the nanowire effects. We have shown that with more generally available and commercialized materials, we can still achieve the results that agree with the Chabinyc Model in Figure 1 of general thermoelectric performance distribution.

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Current Position

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Education

University of Illinois at Urbana-Champaign, 08/2011-12/2014
Major: Bachelor's degree of Science in Physics
Minor: Mathematics

Johns Hopkins University, 08/2016-present
Major: Master in Material Science & Engineering

Research interests

Photovoltaics semiconductors super-conductors
thermoelectric materials electronic material processing
renewable energy technologies Nano materials thin film technologies

Research Experience

Undergraduate School
Undergraduate Researcher in Department of Physics, Summer 2012

- Use C programming to create a code to solve the differential equations

Undergraduate Researcher in Department of MSE, Fall 2014

- Learn the method purification of aligned arrays of single-walled carbon nanotubes (SWNTs) by using nanoscale thermocapillary flows
- Process optimization and design to look for an ideal condition that can completely eliminate metallic single-walled carbon nanotubes (m-SWNTs).
- Used micro-probe station to characterize SWNT devices

Research assistant**,** Spring 2015-Summer 2016

- Use the method of microwave to look for an ideal condition that can completely eliminate metallic single-walled carbon nanotubes (m-SWNTs).
- Use e-beam evaporator to deposit materials on carbon-nanotube samples for purification
- Sample characterization via AFM and SEM
- Use photolithography to create two terminal SWNT devices

Graduate School

Graduate Research Assistant in Department of MSE, Fall 2016-present

- Doping thiophene based polymers with inorganic semiconductors to achieve ultra-high thermoelectric performance (mostly p-type materials, several n-type ones).
- Mixing thiophene based polymers with carbon nano-structures to make devices, and observe their thermoelectric performance.
- Looking for new combinations of organic and inorganic materials to make devices with good thermoelectric performance
- Looking for techniques to improve the thermoelectric performance of existed devices
- Testing the influence of annealing process on thermoelectric performance of different materials.

Publications

"Direct current injection and thermocapillary flow for purification of aligned arrays of single-walled carbon nanotubes", Journal of Applied Physics, 117, 134303 (2015)

"Mechanisms for Performance Enhancement of Bi2Te3 in Polymer Composites" In progress

Technical Skills

Programming

Microsoft Programs (i.e. Excel, Word, etc.) C Programming

Deposition

Thermal evaporator Atomic Layer Deposition (ALD)
E-beam evaporator Spin coating Drop casting

Measurement & characterization

Atomic Force Microscope (AFM) Scanning Electron Microscope (SEM)
Probe station

Surface fabrication

Photolithography Reactive Ion Etch

Other Special

Brush deposition
(self-developed method to make films with sticky solution with very little solvent or with materials that cannot be dissolved in solvent)